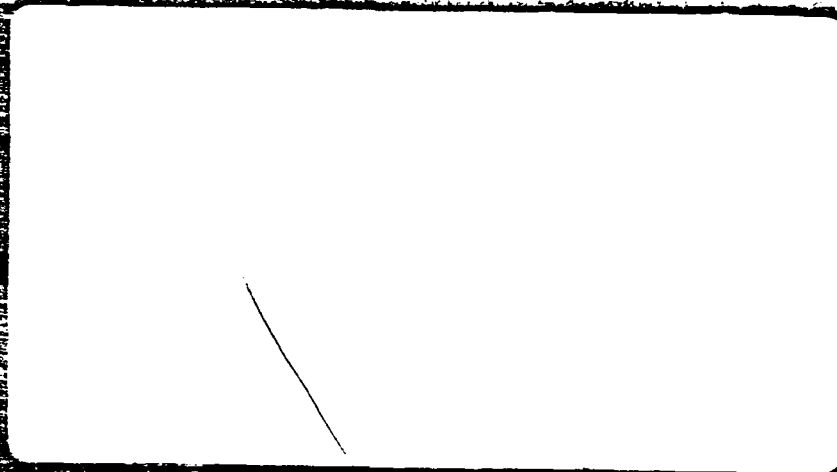


AD-A197 889

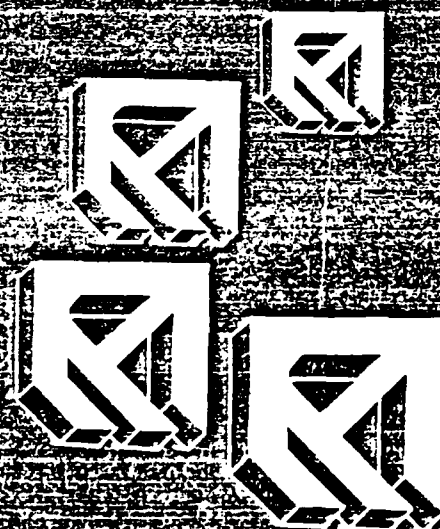
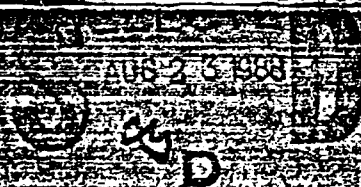
Materials Processing Center

School of Engineering



DTIC

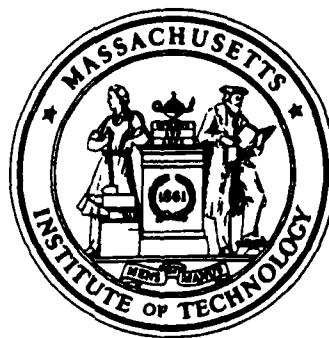
AUG 26 1988



STATEMENT
of WORK
on the
subject of
the
work
of the
center
of the
school
of the
institute

88-8-10-08-3

Massachusetts Institute of Technology



**CERAMICS PROCESSING
RESEARCH LABORATORY**

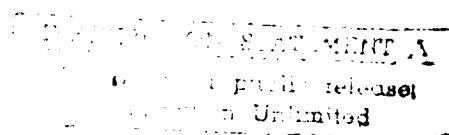
**SYNTHESIS AND PROCESSING OF
CERAMIC SUPERCONDUCTORS**

**Michael J. Cima, Wendell E. Rhine,
and H. Kent Bowen**

DTIC
ELECTE
AUG 23 1988
S D

FINAL REPORT *ND0014-87-K-0736*
on work done under ONR Contract #~~*ND0014-87-K-0736*~~
during the period
July 1, 1987 - July 1, 1988

Submitted to the Office of Naval Research, July 1988.



**Building No. 12
Massachusetts Institute of Technology
Materials Processing Center
Cambridge, MA 02139**

July 1, 1987 – July 1, 1988

per ltr

Synthesis and Processing of Ceramic Superconductors

M.J. Cima, W.E. Rhine, and H.K. Bowen

The discovery of ceramic materials with superconducting transitions above the temperature of liquid nitrogen has continued to attract a great deal of interest for commercial and defense applications. The research supported by ONR Contract #N0014-87-K-0736 has contributed to the growing technical base for fabricating high-temperature superconducting devices. Our findings, supported fully or in part by this contract, have been reported to the scientific community through four publications and one technical presentation [1-5]. Two papers have already appeared in print; two more have been accepted for publication. Copies of these papers can be found at the end of this report.

The results of our research can be categorized into three areas: chemical synthesis, microstructural control, and reactions with substrates. Specific research results are detailed in the included papers, and an interim report on nitrate decomposition chemistry is also included [6].

The program has contributed possibly important results in each of these three areas. Some of the implications of our research are briefly reviewed here, as are some yet unpublished results.

The chemical synthesis of submicrometer, chemically homogeneous $\text{Ba}_2\text{YCu}_3\text{O}_{6.9}$ powder has proven to be the most challenging of the three research areas. In this project, many Cu alkoxides were synthesized but none was soluble enough in common organic solvents to prepare powders by homogeneous nucleation and growth methods. Our success with particle size control [2] through sol-gel emulsion methods prompted us to study the reactions that take place during calcination of the precursor powder. Most chemical routes to powders and films produce material that is amorphous and/or contains constituents not present in the desired product. Heat treatment (calcination) decomposes the precursor material and crystallizes the desired phase.

Most notable of the problems associated with calcination in $\text{Ba}_2\text{YCu}_3\text{O}_{6.9}$ synthesis is carbon retention. Precursor material containing carbon invariably forms BaCO_3 upon calcination. The decomposition of BaCO_3 is typically very slow at 900°C . Common ceramic synthesis methods, such as the Pechini Method or alkoxide hydrolysis, incorporate large amounts of carbon. Even in techniques that do not use hydrocarbon compounds as stoichiometric quantities, carbon is retained from minor constituents or contamination. The sol-gel emulsion synthetic method uses hydrocarbon compounds both as surfactants to stabilize the emulsion and as gellation agents. Figure 1 of Ref. [6] compares the carbon content of precursor powder derived from the sol-gel emulsion method to the carbon content of precursor powder obtained by freeze-drying or spray-drying nitrate solutions of Ba, Y, and Cu of the correct composition to produce BYC. Of course, the carbon content of the emulsion-derived powder is greatly reduced upon calcination, but requires high temperatures.

One of our proposals [7] to investigate alternative chemical routes to reduce the effects of carbon contamination in BYC has shown some success, independent of other investigators [8]. The approach is based on observations made during the fabrication of sputtered films using BaF_2 targets as the barium source. The deposited film is typically an amorphous oxy-fluoride film that must be heat-treated in water vapor to remove the fluorine. Researchers at Bellcore have noted confidentially that the oxy-fluoride precursor film can be patterned by conventional lithographic techniques without degrading the superconducting film. Conversely, films that are already superconducting are irreversibly damaged by lithography. Presumably the barium in the oxy-fluoride film is passivated as BaF_2 during processing and is prevented from reacting.

The incorporation of fluorine into the precursor powder or film might prevent or reduce BaCO_3 formation and thus decrease the temperatures required during calcination. One potential problem is volatilization of copper halides, which has already been noted in our work [2] and can be noticed in the data reported by Gupta et al. [8]. More research is required on this complex chemistry to determine whether carbon can be eliminated from the powder or film before the vapor pressure of CuF_2 becomes too high. This issue and the volatilization of copper during nitrate decomposition [6] are currently under study.

We have shown that cryogenic processing of BYC powders induces texture and may provide a route to textured sintered microstructures [3]. Textured microstructures have proven to be of the utmost importance for high J_c ceramic superconductors. The relationship between the grain boundary misorientation angle and J_c has been measured recently [9] and clearly suggests the need for highly oriented microstructures. Textured microstructures produced by melt processing have also demonstrated improved J_c [10,11]. Unfortunately, in the case of BYC, melting is associated with partial decomposition by incongruent melting, and it has proven very difficult to completely eliminate second phases by low-temperature anneals.

Improvements in critical current densities due to cryogenic texturing have yet to be demonstrated, primarily due to the lack of an available method for consolidating powders in liquid nitrogen. The green densities for textured powder compacts have thus far been too low to produce dense samples. Efforts are currently being made to filter cast or press powder in liquid nitrogen, but this has proved difficult.

A study of the reaction between $2\text{Ba}_2\text{YCu}_3\text{O}_{6.9}$ and yttria-stabilized zirconia [4] may have important implications in many areas of ceramic superconductor technology. The overall chemical reaction can be represented as:



which suggests that BYC films degrade in contact with YSZ by barium diffusion out of the film and into the substrate to form BaZrO_3 , leaving behind a film rich in yttrium and copper. We proposed and demonstrated that BaZrO_3 forms a substrate chemically inert to BYC at 950°C , and have more recently shown that it is stable in contact with BYC melts at 1300°C .

The implications of the work are several-fold. Although pure BaZrO_3 functions as a poor dielectric at high frequencies, CaZrO_3 and SrZrO_3 are used in commercial RF applications. It may be that BaZrO_3 could be used as a diffusion barrier on other zirconates or perhaps on still other dielectrics. The simple technique described by Cima et al. [4] for studying reactions between BYC and YSZ is being extended to other potential substrates by both the CPRL and other groups [12,13] for $\text{Ba}_2\text{YCu}_3\text{O}_{6.9}$ and $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ films. Lastly, because BaZrO_3 is also inert to molten BYC, it is being considered as a crucible material for the solidification processing of textured BYC [13].

REFERENCES

- [1] M.J. Cima and W.E. Rhine, "Powder Processing for Microstructural Control in Ceramic Superconductors," *Adv. Ceram. Mats.*, **2** [38] 329-36 (1988).
- [2] M.J. Cima, R. Chiu, and W.E. Rhine, "Ba₂YCu₃O_{6.9} Powder Preparation by Sol-Gel Emulsion Techniques," *Mat. Res. Soc. Symp. Proc.*, Vol. 99, pp. 241-44 (1988).
- [3] S.C. Peterson and M.J. Cima, "Magnetic Inducement of Texture in Ba₂YCu₃O_{6.9} Particle Assemblies under Cryogenic Conditions," to be published in *J. Am. Ceram. Soc. Commun.*
- [4] M.J. Cima, J.S. Schneider, S.C. Peterson, and W. Coblenz, "Reaction of Ba₂YCu₃O_{6.9} Films with Yttria-Stabilized Zirconia Substrates," to be published in *Appl. Phys. Lett.*
- [5] M.J. Cima, W.E. Rhine, and S. Peterson, "Controlled Microstructure in Ba₂YCu₃O_{6.9} and Its Relation to Electrical Properties," presented at the Fall Meeting of the Electronics Division of the Am. Ceram. Soc., Denver, CO, October, 1987.
- [6] R. Chiu, M.J. Cima, and W.E. Rhine, "Synthesis of Ba₂YCu₃O_{6.9} Powder," CPRL Report #R15, pp. 2-1 - 2-5, June, 1988.
- [7] Presented at meeting with Dr. Kay Rhyne at MIT, April 4, 1988.
- [8] A. Gupta, R. Jagannathan, E.I. Cooper, E.A. Giess, J.I. Landman, and B.W. Hussey, *Appl. Phys. Lett.*, **52**, 2077 (1988).
- [9] D. Dimos, P. Chaudhari, J. Mannhart, and F.K. LaGovesi, submitted to *Phys. Rev. B*.
- [10] S. Jin, T.H. Tiefel, R.C. Sherwood, M.E. Davis, R.B. van Dover, G.W. Kammlott, R.A. Fastnacht, and H.D. Keith, "High Critical Currents in Y-Ba-Cu-O Superconductors," *Appl. Phys. Lett.*, **52** [24] 2074-76.
- [11] R.S. Fiegulson, D. Gazit, D.K. Fork, and T.H. Geballe, *Science*, **240**, 1642 (1988).
- [12] Prof. D. Rudman, MIT, private communication.
- [13] Prof. H. Brody, Univ. Pittsburgh, and Prof. M. Flemings, MIT, private communication.

Powder Processing for Microstructural Control in Ceramic Superconductors

M.J. Cima, W.E. Rhine

Ceramics Processing Research Laboratory,
Materials Processing Center
Massachusetts Institute of Technology
Cambridge MA 02139

Along with fine grain sizes to increase the structural integrity of ceramic parts, control of the microstructure in samples of the new ceramic cuprates will be necessary to make possible experiments designed to reveal structure-property-processing relationships, i.e., relationships between microstructure, critical current density, and magnetic field. The low critical current densities of existing polycrystalline samples can originate in such properties as:

- a) the critical importance of stoichiometry on a macro- and microscale, particularly with respect to stoichiometry-driven crystal defects
- b) extreme anisotropy, which necessitates percolative current paths in randomly oriented polycrystalline materials
- c) microcracking at the grain boundaries
- d) highly resistive grain boundaries, at least for some orientations
- e) the lack of classical grain-boundary pinning phenomena, similar to that observed in lower-temperature superconductors

If stoichiometry, grain size, crystallographic texture, and, in general, ceramic microstructure can be controlled, these questions could perhaps be resolved. We believe, based on past history and present advanced ceramics processing capabilities, that the technically important properties for ceramic superconductors will be substantially improved by this approach and that, perhaps more importantly, a technology base for the manufacture of these new superconductors will be established.

Key to the production and control of ceramic microstructures is the control of their starting powder characteristics and the microstructure of the greenbody. Such control is not currently practiced in the preparation of the new ceramic superconductors. The method most often used to prepare superconducting cuprates involves the solid-state reaction between Y_2O_3 , CuO , and $BaCO_3$. In this method, decomposition of the $BaCO_3$ appears to be the rate-limiting step. The calcination temperature must be high enough to obtain a significant decomposition rate of the carbonate but below the temperature at which sintering is to be performed to produce an active powder for sintering. The sintering temperature must in turn be below the temperature at which incongruent melting occurs (between 1000 and 1025°C for $Ba_2YCu_3O_{6.8}$). TGA experiments show that carbonate decomposition does not occur at a significant rate below 925°C, thus there is only a limited region over which the calcination can be performed. Figure 1 depicts the mass loss as a function of time for the calcination of 300

gm of BaCO_3 , CuO , and Y_2O_3 at 950°C . We observed significant inhomogeneous reaction when preparing large amounts of the cuprate. The powder near the surface of the powder bed would quickly acquire the black color associated with $\text{Ba}_2\text{YCu}_3\text{O}_{6.8}$ but the rest of the powder would be green, characteristic of the resistive phases in the ternary system. Intermediate milling and minimizing the thickness of the powder bed was performed in order to speed the process and produce chemically homogeneous powder. Obvious alternates to this procedure would be to use rotary calcination or to use barium oxide as the barium source; however, working with high surface area barium oxide on a large scale can present problems because it is hygroscopic and an irritant.

The solid state reaction methods do not allow for sufficient control of the powder morphology to produce dense samples upon sintering. Figure 2 depicts a fracture surface of a sample prepared from calcined powder of $\text{Ba}_2\text{YCu}_3\text{O}_{6.8}$ isopressed followed by sintering in oxygen for 12 h at 950°C . It is clear from the figure that the sample is very porous and possesses very large grains. The mechanical integrity of specimens produced in this way is very poor and a fracture surface for microscopic examination may be frequently produced by hand.

Advances in ceramics processing have been made by the successful application of colloidal processing techniques. Efficient milling and classification of ceramic powders can be achieved by dispersing the powder in a liquid medium. The "slip" thus formed must be stabilized by the presence of a dispersant that prevents flocculation of the particles. Various colloidal consolidation methods, such as colloidal pressing, filter casting, or centrifuge casting, have been used to produce controlled and reproducible greenbody microstructures for sintering studies (Roosen and Bowen 1986).

Dispersion in high dielectric media, such as water, is routinely achieved by electrostatic stabilization which arises through the selective adsorption on the particles of small amounts of ionic species dissolved in the electrolyte. Water can not be used as the dispersing medium for $\text{Ba}_2\text{YCu}_3\text{O}_{6.8}$ powders because of the now widely recognized corrosion reaction that occurs between water and this material. Thus, cuprate processing requires organic solvents as the dispersing medium. Stabilization in low dielectric constant media is frequently achieved by adsorption of molecules on the particle surface. The adsorbed molecules prevent close approach of two particle surfaces through steric repulsion. Our observations indicate that OLOATM1200 (Chevron Chemical Co., Oronite Additives Div., San Francisco) is very effective at dispersing cuprate powders in hexane. The chemical structure of OLOA 1200 (Figure 3) has recently been determined (Wiseman, 1985) and consists of an isobutylene polymer bonded to an organic amine through a succinimide group. The polymeric end of the molecule undoubtedly provides the solubility in hexane and steric repulsion required from the dispersant, while the polar amine end increases the adsorption coefficient of the dispersant on the powder surface through interaction with surface acid sites. In some powder systems OLOA 1200 stabilization is thought to include both steric and electrostatic stabilization in low dielectric media through reaction with Bronsted acid sites on the surface of the powder (Bishop, 1986; Pugh, Matsunaga, and Fowkes, 1983; Pugh and Fowkes, 1984). We have not yet characterized the contribution of electrostatic stabilization in the cuprate-heptane-OLOA system.

We have succeeded in producing high density cuprate samples by application of the colloidal processing methods discussed above. The samples were prepared by milling a slip consisting of cuprate powders, produced by solid state reaction, dispersed with OLOA in hexane, for 48 hrs with zirconia mixing balls. The slurry was sedimentation classified to remove the largest agglomerates by decanting the top portion of the slip after waiting 15 minutes for the largest. The resulting slip of the fines was centrifuge-cast and fired for 12 h in oxygen at 950°C. Figure 4 shows a fracture surface of $\text{Ba}_2\text{YCu}_3\text{O}_{5.9}$ produced by this procedure. The $\text{Ba}_2\text{YCu}_3\text{O}_{5.9}$ final material is greater than 90% of theoretical density and has a uniform grain structure. Fracture surfaces had to be produced by impact with a hammer. The mechanical strength of the high density material clearly exceeds that of samples prepared by dry-pressing the calcined powder and firing, due to the classified powder compacts' increased density and finer microstructure.

We have observed differences in the electrical behavior of high density samples and those samples produced by conventional means. Figure 5 shows the results of a four point a.c. electrical resistance experiment as a function of temperature. The response shows the now widely-recognized linearly decreasing resistance down to 93K where the superconducting transition occurs and is reversible upon warming. The low density samples can exhibit hysteresis in their electrical response (see Figure 6) and show abrupt transitions at temperatures higher than 93K. Although there has been widespread speculation that such features represent some portion of the sample becoming superconducting, we feel that in our samples these features result from poor mechanical integrity since they seem only to be present in samples of low density. We are actively pursuing critical current density measurements designed to reveal if any improvement can be derived from the increased density of the material.

The difficulties in preparing chemically homogeneous submicron sized particles from solid state reactions provides the impetus for seeking alternate chemical routes that will allow control of the particle morphology. Several classical methods, as well as new techniques, have been examined in our preliminary study.

We, as well as other researchers, have investigated the coprecipitation of oxalates as a lower temperature route to the cuprates. Thermogravimetric results indicate that the oxalates decompose to the oxides below 500°C. We have had great difficulty, however, in stoichiometric precipitation from barium, yttrium, and copper solutions. The supernatant contains unprecipitated copper when excess oxalic acid used.

One method that has shown great promise for synthesizing narrow-sized, submicron powders is the hydrolysis of hydrolytically unstable precursors such as the metal alkoxides. Published papers and our preliminary results indicate that this approach will require considerable effort to prepare superconducting cuprate powders since all of the copper (II) alkoxides reported to date are insoluble in common organic solvents. The few preliminary experiments that have been conducted in this laboratory indicate that at least partially soluble derivatives can be prepared. On the other hand, copper (I) alkoxides are soluble and can readily be oxidized to CuO . Therefore, Cu(I) compounds may be better precursors than Cu(II) compounds.

Exciting evidence obtained from our recent work suggests that the emulsion state offers opportunities for synthesizing spherical powders with complex compositions. For example, narrow-sized, unagglomerated SiO_2 powders have been synthesized from TEOS under acidic conditions, and yttrium-aluminate powders have been synthesized by combining sol-gel and emulsion techniques. The latter example (Gowda and Bowen, 1986) offers the advantage that complex compositions can be prepared from inexpensive precursors. For example, we have synthesized $\text{Y}_{1.2}\text{Ba}_{0.8}\text{Cu}(\text{OH})_x$ by preparing an emulsion of an aqueous solution of Y, Ba, and Cu salts in heptane and coprecipitating the hydroxides in the emulsion droplets (microreactors) by bubbling ammonia through the emulsion. The procedure is outlined in Figure 7. Various industrial surfactants such as those made from partial esters of fatty acids and sorbitol, or polyoxyethylene ethers of fatty alcohols are used to stabilize the emulsion which is formed by sonication. In this particular experiment, spherical particles were prepared with diameters between 1 and 3 micrometers (Figure 8).

New results indicate that high-molecular-weight amines can be used instead of ammonia. These amines can be used to extract counter-ions (used to form the aqueous sol) into the organic phase. Nitric acid, for example, can be extracted from a nitrate solution of copper, barium and yttrium. Through the extraction of the acid, the pH of the aqueous phase is raised so that the hydrous oxides of the cations precipitate to form an amorphous gel. The advantage of this method is that the counter-ions are not precipitated along with the cations. This may allow preparation of the sol from chloride solutions which can be made much more concentrated than other solutions. Excess chloride ions are difficult to remove due to the high stability of metal oxychlorides, or may result in depletion of copper from the oxide when fired because of the high vapor pressure of copper chloride. The method is successful at producing powders of the correct phase after calcination but has not yet been scaled up to prepare large quantities for sintering.

Acknowledgement

Special thanks to Prof. D. Rudman and Prof. R. Rose for their advise and help with measurements.

References

- B. Bishop; to be submitted to *Advanced Ceramic Materials*, 1987
- G. Gowda, H.K. Bowen, *Ceramics Society Meeting*, New Orleans, 1986
- R.J. Pugh, T. Masunaga, F.M. Fowkes; *Colloids and Surfaces*, 7, 183-207 (1983)
- R.J. Pugh, F.M. Fowkes; *Colloids and Surfaces*, 9, 33-46 (1984)
- A. Roosen, H.K. Bowen; submitted to *Amer. Ceram. Soc. Bull.* 1987
- G. Wiseman; unpublished research

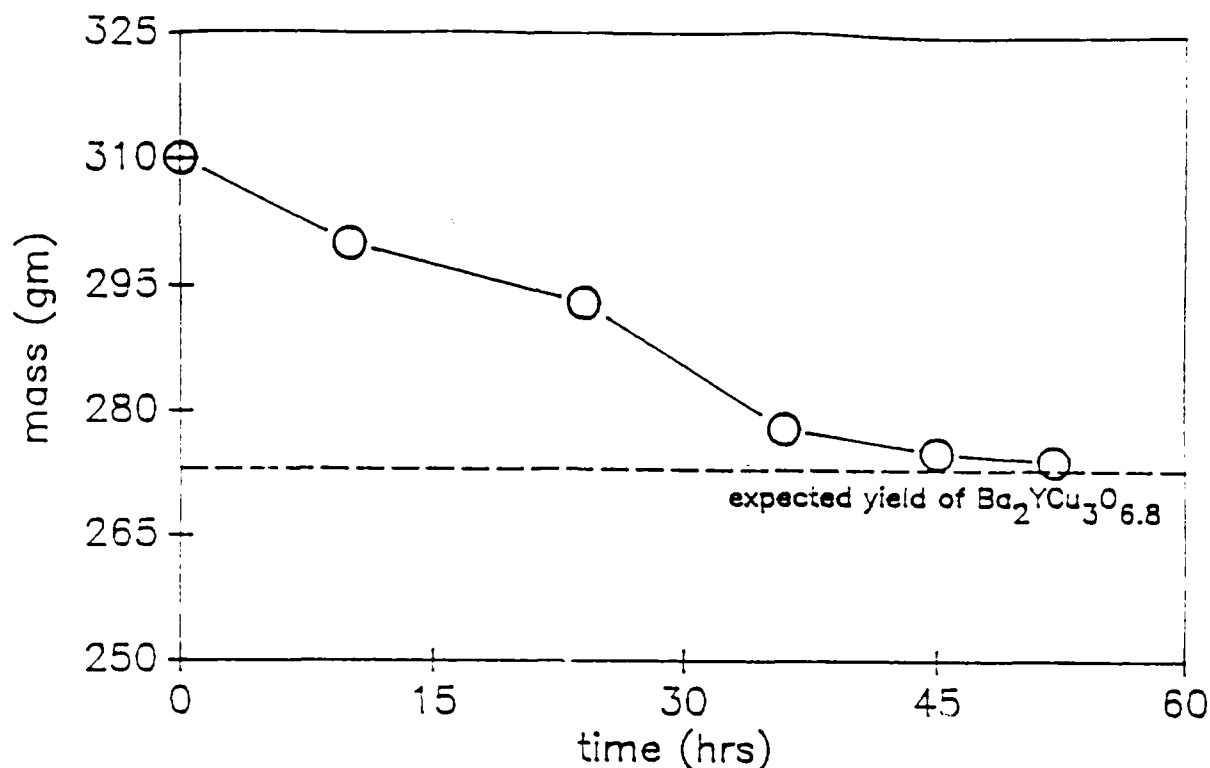


Figure 1: Reaction of Y_2O_3 , CuO and $BaCO_3$ in air at $950^\circ C$.

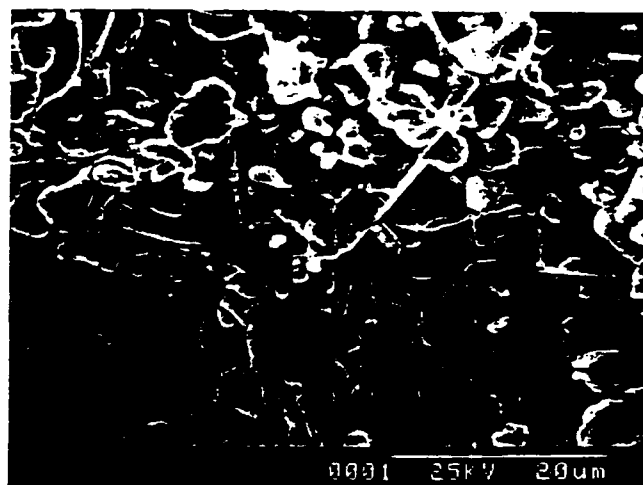


Figure 2: Fracture surface of $Ba_2YCu_3O_{6.9}$ sintered in oxygen for 12h at $950^\circ C$. Sample was prepared from calcined powder without the use of colloidal processing methods.

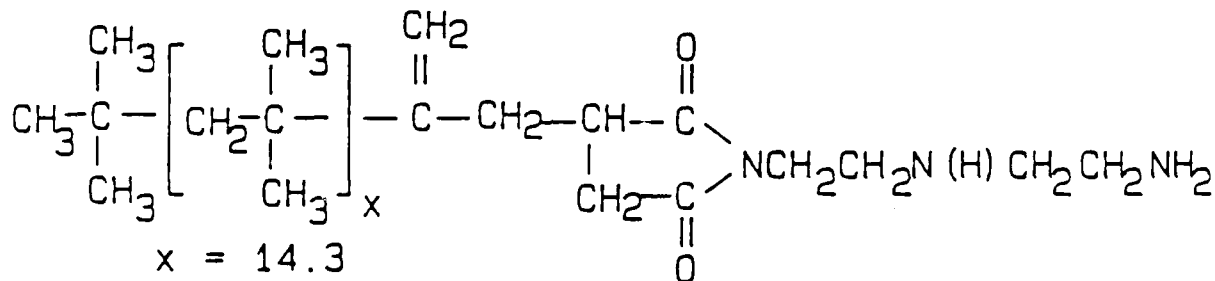


Figure 3: Chemical structure of OLOATM1200.

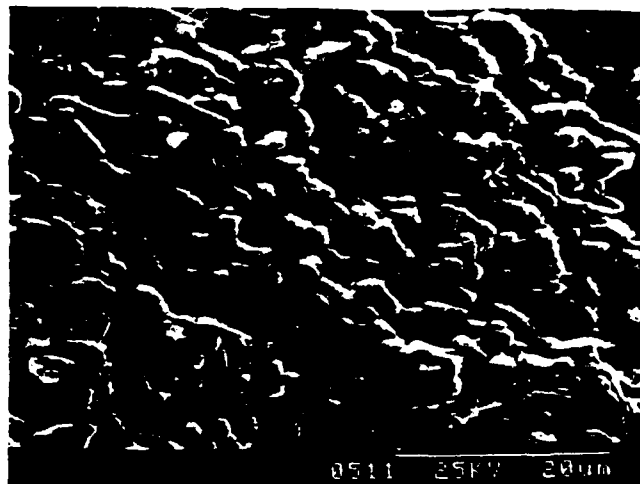


Figure 4: Fracture surface of $\text{Ba}_2\text{YCu}_3\text{O}_{6.9}$ prepared by colloidal processing techniques and sintered in oxygen at 950°C for 12h.

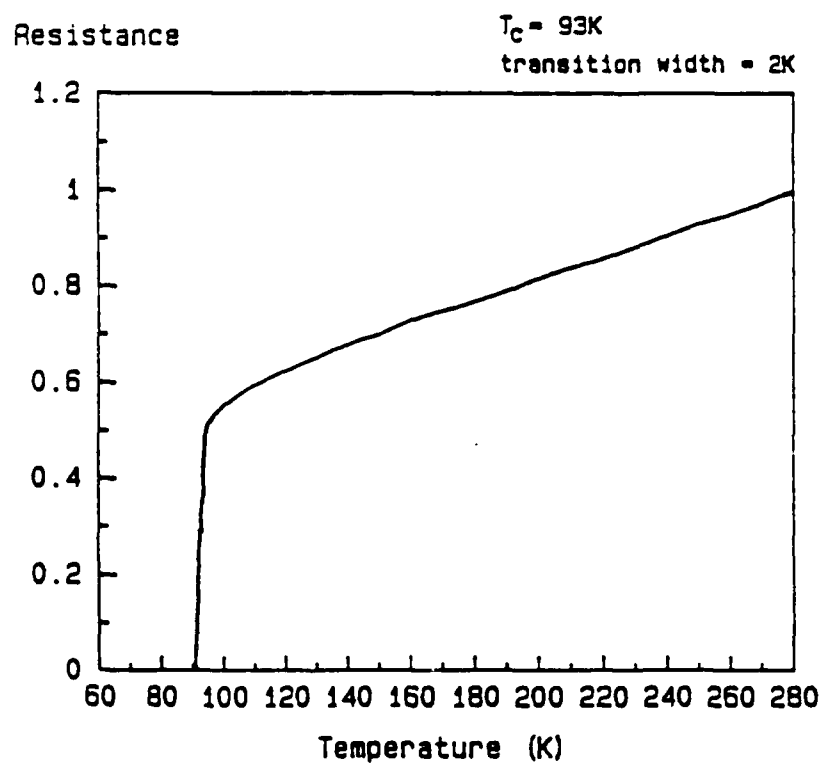


Figure 5: Resistance versus temperature for a high density sample of $\text{Ba}_2\text{YCu}_3\text{O}_{6.9}$.

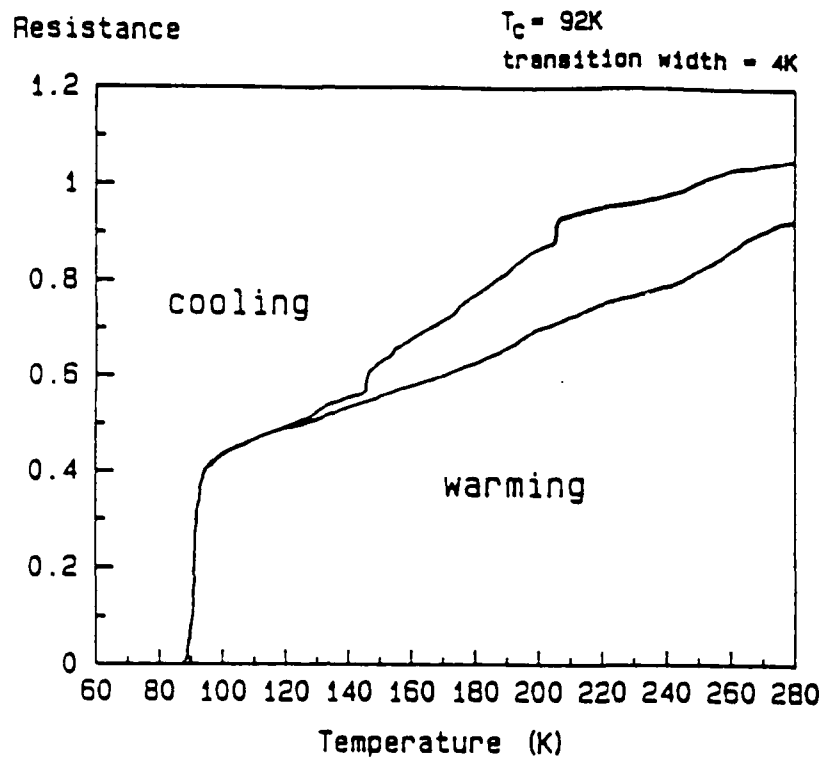


Figure 6: Resistance versus temperature for a low density sample of $Ba_2YCu_3O_{5.9}$.

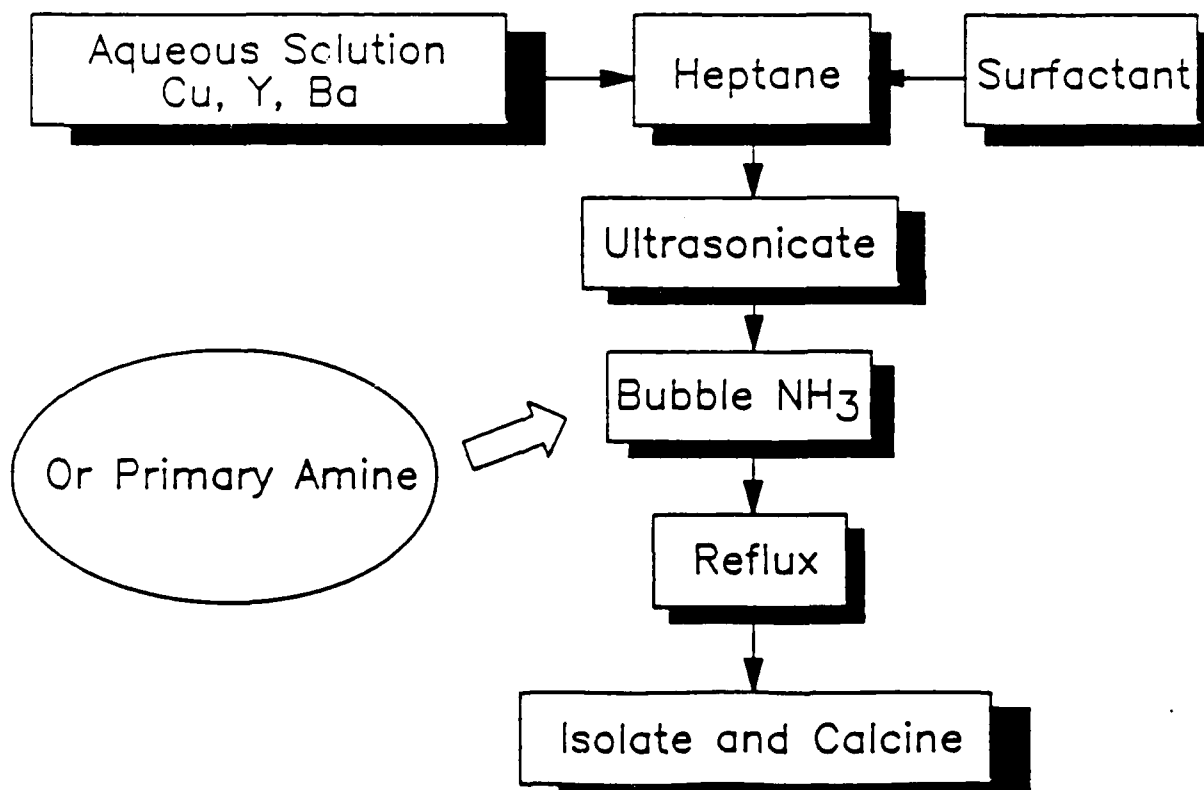


Figure 7: Processing procedure for emulsion sol-gel powder preparation.

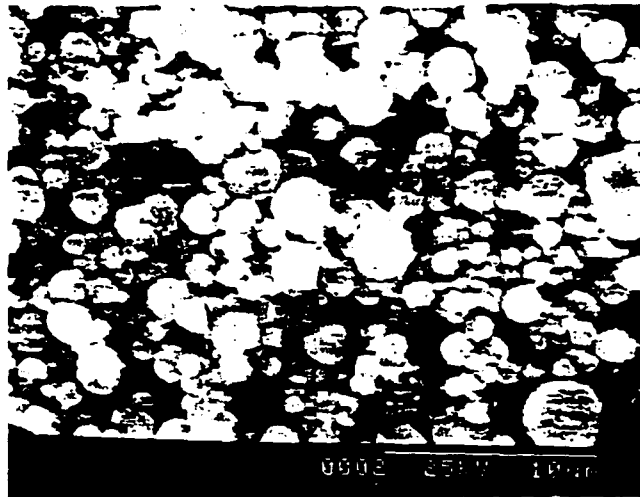


Figure 8: Powder prepared by combining sol-gel and emulsion techniques. The material shown has the composition $Y_{1.2}Ba_{0.8}Cu(OH)_x$.

$\text{Ba}_2\text{YCu}_3\text{O}_{6.9}$ POWDER PREPARATION BY SOL-GEL EMULSION TECHNIQUES

M.J. Cima*, R. Chiu*, and W.E. Rhine*

*Ceramics Processing Research Laboratory, Materials Processing Center,
Massachusetts Institute of Technology, 77 Massachusetts Ave., Cambridge, MA
02139

Research support from the Defense Advanced Research Projects Agency

ABSTRACT

Barium yttrium cuprate powders were prepared by a sol-gel emulsion process in which an aqueous nitrate solution containing Ba, Y, and Cu in the correct stoichiometry was emulsified in heptane. The resulting micrometer-sized droplets were gelled by adding a high-molecular-weight primary amine that extracts nitric acid from the aqueous phase and raises the pH of the droplets. Thermal gravimetric analysis revealed that the correct overall stoichiometry was obtained at temperatures lower than 400°C during calcination, but X-ray diffraction showed that calcination at temperatures greater than 800°C may be required to produce the correct phase. One possible advantage of this technique is the control of powder morphology on a micrometer scale so that powders can be prepared for advanced ceramics processing methods. Also, segregation of components, if any, will be restricted to distances less than one micrometer.

INTRODUCTION

A necessary step for controlling ceramic microstructures is controlling the starting powder's characteristics. From a ceramics-processing perspective there are clear advantages for the use of submicrometer, chemically homogeneous powders. These powders, if consolidated correctly, will make controlled microstructures possible and permit a reduction in sintering temperature. Such a reduction may reduce the amount of reaction observed when $\text{Ba}_2\text{YCu}_3\text{O}_{6.9}$ (BYC) is fired on substrates for the production of thick-film superconducting devices or signal lines. A lower sintering temperature will also increase the total oxygen content of monolithic BYC pieces after sintering and decrease the time needed at low temperature to fully oxidize the sample [1].

The method most often used to prepare superconducting cuprates involves the solid-state reaction between Y_2O_3 , CuO , and BaCO_3 [2]. This method does not permit control of particle morphology, and the decomposition of BaCO_3 , the rate-limiting step, requires calcination temperatures in excess of 900°C. This paper describes a simple and inexpensive route for the production of submicrometer BYC powders based on the concept of converting emulsion droplets into particles.

Emulsion synthesis techniques for ceramic powders have been investigated for some time. Previous research in this area has concentrated on synthesizing simple compositions with a single cation [3-9]. Recently yttrium-aluminate powders have been synthesized by combining sol-gel and emulsion techniques [10]. In this case ammonia is used to raise the pH of an aqueous sol solution in an organic continuous phase; this combination allows the production of complex compositions from inexpensive precursors.

In a slightly different approach, ammonia is replaced with a high-molecular-weight amine as the base [9]. These amines extract counter-ions (used to form the aqueous sol) into the organic phase. Nitric acid, for example, can be extracted from a nitrate solution of copper, barium, and yttrium. As the acid is extracted, the pH of the aqueous phase is raised and the hydrous oxides of the cations precipitate to form an amorphous gel.

EXPERIMENTAL PROCEDURE

An aqueous nitrate sol was prepared by dissolving stoichiometric amounts of barium nitrate, copper nitrate, and yttrium nitrate in a minimum amount of water. An aqueous chloride sol was prepared in the same way, except with chloride salts. Since both yttrium chloride and yttrium nitrate are hygroscopic it is difficult to obtain accurate amounts of these yttrium salts. We prepared these yttrium chloride and nitrate salts by reacting yttria (Y_2O_3) with concentrated hydrochloric acid or nitric acid, respectively. Ten parts of the aqueous sol were then dispersed in a continuous heptane phase using one part surfactant (Span®80 and Brij®30 in a 2:1 mass ratio; both from ICI Americas Inc., Wilmington, DE). The surfactants were added to the organic phase before the addition of the sol. The sol concentrations studied were 10 vol% for the nitrates and 5 vol% for the chlorides. The mixture was then ultrasonically agitated to form an emulsion.

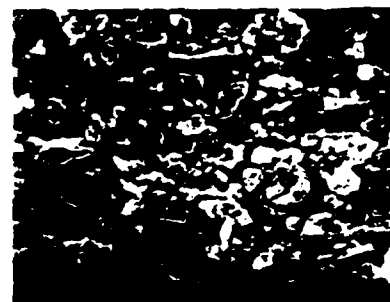
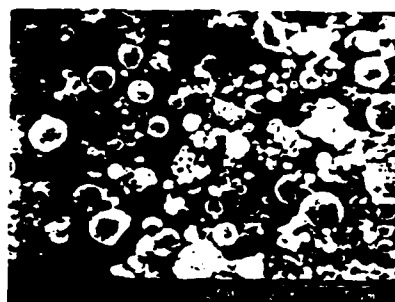
The emulsified mixture was gelled by adding the gelation agent Primene-JMT (Rohm and Haas Co., Philadelphia, PA), a high-molecular-weight primary amine. Since Primene-JMT had not yet been characterized, it was added in excess (500 mol%). After the gelled particles settled, the heptane was decanted. The resulting gel was then refluxed in heptane; a Dean-Stark trap was used to remove the water. The refluxed, dried powder was washed and centrifuged with hexane 4 times before it was air dried and calcined.

The powders were then characterized. Particle morphology was studied by scanning electron microscopy (SEM), and thermal gravimetric analysis (TGA) was performed at a heating rate of $2^\circ\text{C}/\text{min}$ to 250°C and $5^\circ\text{C}/\text{min}$ to 950°C . Powders calcined at 400, 600, 800, and 950°C were examined by X-ray diffraction (XRD) with a CuK α and Ni filter. Finally, a sample of the powder calcined at 950°C was sintered in oxygen and tested for critical temperature using a DC four-point probe measurement.

RESULTS AND DISCUSSION

Typically, the higher the salt concentration in the sol, the easier it is to retain the particle morphology following the gelation process. In this study the concentration of the aqueous chloride sol was 4 times that of the nitrate. The SEMs of Figure 1 compare chloride- and nitrate-sol derived powders. To increase the concentration of the nitrate sol, the gelation process was carried out at a higher temperature ($60-70^\circ\text{C}$), which doubled the concentration of salts in the sol. The resulting powder (Fig. 2) shows a significant improvement.

Residual chloride in the gelled chloride-derived powder was difficult to remove. This could be because copper halides are volatile at temperatures below the calcination temperature, or because metal oxyhalides



a

b

Figure 1. SEMs of a) chloride- and b) nitrate-derived powder.

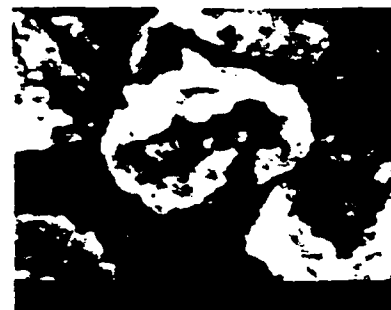


Figure 2. SEM of nitrate-derived powder gelled at high temperature.

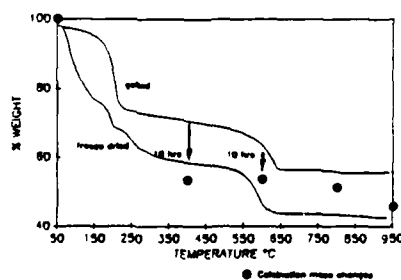


Figure 3. TGAs of freeze-dried and gelled nitrate-derived powder. Filled circles are weight loss from 10 h calcination. At 950°C, the weight loss was lower than actual since powder was physically lost during the 200°C reaction.

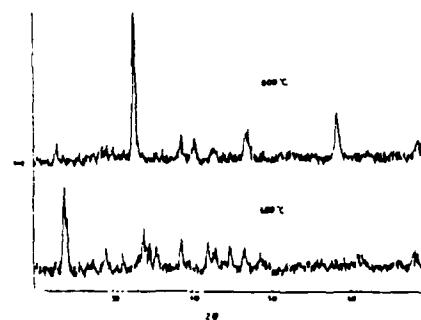


Figure 4. XRDs of nitrate-derived powder calcined at 600 and 800°C.

are very stable. We observed a small amount of material condensing at the top of our MgO crucibles, and using qualitative analysis with silver nitrate detected chloride in the final product. XRD of the product also indicated that BYC was not present.

Figure 3 compares TGAs for a nitrate-derived powder and a powder produced by freeze drying an aqueous solution of the nitrate salts. Because there are differences in hydration the total weight losses are different, but the reactions at 200 and 600°C are clearly present in each TGA.

The TGA results suggest that the correct stoichiometry may be obtained at calcination temperatures lower than 400°C. XRD results for the sample calcined at 400°C for 10 hours, however, showed only weak patterns tentatively indexed as small amounts of barium carbonate, copper oxide, and yttria. At temperatures between 600 and 800°C, the correct phase is indeed produced, as shown in Figure 4. The formation of barium carbonate is probably due to residual organic surfactant or the primary amine. From the calcination study, the maximum amount of barium carbonate detected was less than one third of that which would have been present if all of the barium were in the carbonate form.

A resistivity measurement of a sintered sample of the final product was made. The transition temperature was 93K with zero resistivity at 88K based on a 2 nanovolt/cm criterion for superconductivity at 1 milliamperes.

REFERENCES

1. M.J. Cima, presented at the 1987 Am. Cer. Soc. Meeting, Denver, CO, Oct. 1987 (unpublished).
2. M.J. Cima and W.E. Rhine, *Adv. Cer. Mat.* 2 (3b), 329 (1987).
3. A. Hardy, T. McMahon, G. Gowda, R. Riman, W.E. Rhine, and H.K. Bowen, presented at the 3rd Int. Ultrastructure Conf., San Diego, CA, Feb. 1987 (unpublished).
4. P. Reynen, H. Bastius, and M. Fiedler, in *Ceramic Powders*, edited by Vincenzini (Elsevier Science Publishers, Amsterdam, The Netherlands, 1983), pp. 499-504.
5. J.L. Kelley, A.T. Kleinstaubert, S.D. Clinton, and O.C. Dean, *Indust. Eng. Chem. Proc. Des. and Dev.* 4 (2), 212 (1965).
6. P.A. Hass and S.D. Clinton, *Indust. Eng. Chem. Proc. Des. and Dev.* 5 (3), 236 (1966).
7. P.A. Hass, S.D. Clinton, and A.T. Kleinstaubert, *Can. Chem. Eng.* 1966, 348.
8. J.L. Woodhead, *Sci. of Ceramics* 4, 4, 105 (1968).
9. J.L. Woodhead, *Sci. of Ceramics* 4, 4, 105 (1968).
10. G. Gowda and H.K. Bowen, presented at the Am. Cer. Soc. Basic Sci. Div. meeting, New Orleans, 1986 (unpublished).

Magnetic Inducement of Texture in $\text{Ba}_2\text{YCu}_3\text{O}_{6.9}$
Particle Assemblies under Cryogenic Conditions

SIMONE C. PETERSON* and MICHAEL J. CIMA*

Ceramics Processing Research Laboratory, Materials Processing Center,
Massachusetts Institute of Technology, Cambridge, MA, 02139

The properties of $\text{Ba}_2\text{YCu}_3\text{O}_{6.9}$ in the superconducting state and anisotropic behavior can be used to texture polycrystalline samples. Application of a relatively small magnetic field while a particle assembly is immersed in liquid nitrogen preferentially orients the particles so that their c-axis is perpendicular to the direction of the applied field.

I. Introduction

The anisotropic crystal structure of $\text{Ba}_2\text{YCu}_3\text{O}_{6.9}$ (BYC) created speculation that microstructures with preferred crystallographic orientation would improve the low critical current densities characteristic of polycrystalline BYC.¹ Deformation techniques similar to those used to produce textured microstructures in metals have been successfully used for BYC,² but have the disadvantages of restricting the sample shapes that can be produced and requiring long heat treatments to fully oxidize the BYC.

Textured microstructures using non-deformation powder techniques (e.g., applying a magnetic field during consolidation of the greenbody) are common in the production of ferrite magnets. Several recent studies have described efforts to align BYC particles in magnetic fields. Farrell et al.³ showed that single-crystal BYC would align in the presence of a very large magnetic field (9.4 T). Arendt et al.⁴ observed that texture developed in BYC powder placed in a hardening epoxy resin and exposed to fields between 1.5 and 8 T. These studies were performed at room temperature while the powder was in its normal state. The presence of

*Member, the American Ceramic Society

forces that can orient the crystallites is attributed to anisotropy in the magnetic susceptibility.

This paper reports the successful production of texture in powder and sintered microstructures by applying a magnetic field while the specimen is in the superconducting state. Similar observations have recently been made with loose powders at fields lower than those required at room temperature.^{5,6}

II. Experimental Procedure

BYC powder was produced by calcining BaCO_3 , Y_2O_3 , and CuO at 950°C in oxygen. Intermediate milling was performed in hexane between further calcination treatments until the reaction was complete. To produce the proper oxygen content in the powder, a final heat treatment at 700°C was performed in high-purity oxygen, followed by a slow cool to room temperature.

The powder was put into specially designed sample holders, each consisting of a shallow dish 14 mm x 18 mm x 1.5 mm milled into a 32 mm x 25 mm x 4.5 mm piece of acrylic plastic. The powder was made level with the flat upper surface of the dish, which served as the reference plane for both the applied magnetic field and subsequent x-ray diffraction. The design of the holder permitted registration of this surface with the diffractometer axis in a Norelco x-ray diffractometer.*

The holders were placed individually into capped polypropylene tubes modified to allow filling with liquid nitrogen and evaporation of the liquid nitrogen as the sample warmed. Some samples were isolated from the liquid nitrogen by glass cover slips secured with vacuum grease and rubber bands.

*Philips Electronics Instruments, Mahwah, NJ.

Each sample in its holder was oriented in a polypropylene tube (the sample surface could be rotated at angles of up to 45 degrees with respect to the field direction without disturbing the powder). The tube was then placed between the poles of a calibrated DC magnet[&] and filled with liquid nitrogen, and the sample was allowed to cool to the liquid nitrogen temperature. The magnetic field (10-kG (1 T), uniform to within 1% over a dimension five times the diameter of the sample) was then turned on. The liquid nitrogen level was maintained for the first 2 min in the field, then allowed to fall over the next 8 min, after which time the field was reduced once more to 0 kG. The sample was then removed and x-rayed (without the cover slip) at room temperature.

For the powder samples that were to be sintered, the powder-filled holder was inverted onto a MgO sheet. The whole assembly was then immersed in liquid nitrogen in a field. The powder cake left after removing the sample holder was sintered at 950°C for 4 h and furnace cooled in oxygen.

III. Observations

Preferred orientation, induced when the powder surface is prepared, is a major source of intensity errors in x-ray diffraction. Therefore the effects of surface preparation were carefully examined using the control specimens described in Table I. Samples prepared with or without cover slips developed no preferential orientation unless they were exposed to a field while immersed in liquid nitrogen.

Figure 1 depicts the diffraction patterns for three representative samples. Patterns from samples exposed to the field at room temperature were identical to those from unexposed samples at room temperature.

[&]O.S. Walker Co., Inc., Worcester, MA.

Patterns from unexposed samples treated in liquid nitrogen were identical to those from unexposed samples at room temperature.

Application of a field while the samples were immersed in liquid nitrogen created pronounced texturing. When the field was applied parallel to the surface of the powder bed (defined as 0° rotation), an increase in the relative intensity of the 00L reflections was observed. The 007 reflection, which had a relative intensity of 2% in the randomly oriented powder, was most notable. The effect was highly reproducible: it was not a function of the way the powder was placed in the sample holder or whether or not a cover slip was used. Rotation of the powder surface to 45° with respect to the field resulted in a decrease in the relative intensities of the 00L reflections.

The increase in the intensity of the 00L reflections at 0° rotation indicates that the a-b planes of the particles rotate to contain the field vector. Our observation is thus consistent with the conclusion that when BYC particles are in the superconducting state, the c-axis aligns perpendicular to the applied field. Since the fields used in this study were much smaller than those used to obtain texture at room temperature, it is unlikely that the alignment was due to susceptibility variation.

There are two possible sources of force, related to the superconducting properties of the particles, that would make the particles rotate in the field: electronic anisotropy and shape anisotropy. In both cases the particles would rotate to minimize the magnetization.

The Gibb's energy for the orientation of a superconducting particle is minimized when the smallest magnetic moment is generated. Dinger et al.⁷ have shown that large BYC single crystals have extreme magnetization variation with crystallographic orientation. They found the greatest

magnetization and hysteresis for orientations in which the c-axis was parallel to the field; magnetization and hysteresis were drastically reduced when the c-axis was perpendicular to the field. Thus, anisotropy in the irreversible magnetization would account for the texture observed in our experiments.

The second contribution to the force, shape anisotropy, could arise from the shape of the particles. Scanning electron micrographs (SEMs) of the powders in this study show a pronounced plate-like appearance of the individual grains, commonly observed in the calcined powders and microstructures of dense BYC polycrystalline samples. The low-energy surface of the crystal is the 001 face, which is therefore favored in the growth of the particle. The minimum magnetization of such shapes made of an isotropic superconductor is achieved when the 001 face is parallel to the field. Therefore, particle shape may also contribute to the texturing behavior we observed.

Similar observations by other investigators^{5,6} confirm our findings. These investigators used fields of 0.5 T and 1.5 T, respectively, to achieve textures that do not appear to be as pronounced as the texture we observed. In our work texture was maintained in the sintered sample, but because of the sample's low green density the fired body had a very low final density. Steps are being taken to permit consolidation at cryogenic temperatures.

Acknowledgements: The authors are indebted to Prof. Robert Rose and Prof. David Rudman for their advice. The support for this research was provided by the National Science Foundation, the Defense Advanced Research Projects Agency, and the MIT-Industry Ceramics Processing Research Consortium.

References

- ¹S. Jin, R.C. Sherwood, T.H. Tiefel, R.B. van Dover, R.A. Fastnacht, S. Nakahara, M.F. Yan, and D.W. Johnson, "Critical Current Density of the $\text{Ba}_2\text{YCu}_3\text{O}_{7-x}$ Superconductor as Affected by Processing and Microstructural Control," Fall Materials Research Society Meeting, Boston, MA, 1987.
- ²I-W. Chen, X. Wu, S.J. Keating, C.Y. Keating, P.A. Johnson, and T.-Y. Tien, "Texture Development in $\text{YBa}_2\text{Cu}_3\text{O}_x$ by Hot Extrusion and Hot-Pressing," J. Am. Cer. Soc., 70 [12] C388-C390 (1987).
- ³D.E. Farrell, B.S. Chandrasekhar, M.R. DeGuire, M.M. Fang, V.G. Kogan, J.R. Clem, and D.K. Finnemore, "Superconducting Properties of Aligned Crystalline Grains of $\text{Y}_1\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$," Phys. Rev. B, 36 [7] 4025-27 (1987).
- ⁴R.H. Arendt, A.R. Gaddipati, M.F. Garbaskas, E.L. Hall, H.R. Hart, Jr., K.W. Lay, J.D. Livingston, F.E. Luborsky, and L.L. Schilling, "Aligned Sintered Compacts of $\text{RBa}_2\text{Cu}_3\text{O}_{7-x}$ (R = Dy, Er, Eu, Gd, Ho, Y)," Fall Materials Research Society Meeting, Boston, MA, 1987.
- ⁵S.A. Solin, N. Garcia, S. Vieira, and M. Hortal, "Field-Induced Orientation of Nonlevitated Microcrystals of Superconducting $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$," Phys. Rev. Lett., 60 [8] 744-747 (1988).
- ⁶J.M. Tranquada, A.I. Goldman, A.R. Moodenbaugh, G. Shirane, S.K. Sinha, A.J. Jacobson, and J.T. Lewandowski, "Observation of Alignment of Superconducting $\text{YBa}_2\text{Cu}_3\text{O}_7$ Particles in a Magnetic Field Using Neutron Diffraction," Phys. Rev. B, 37 [1] 519-521 (1988).
- ⁷T.R. Dinger, T.K. Worthington, W.J. Gallagher, and R.L. Sandstrom, "Direct Observation of Electronic Anisotropy in Single-Crystal $\text{Y}_1\text{Ba}_2\text{Cu}_3\text{O}_{7-x}$," Phys. Rev. Lett., 58 [25] 2687-90 (1987).

Table 1. Experimental conditions for cryogenically textured specimens.

Sample #	Cover Slip	Temp. (K)	Applied Field (KG)	Rotation in Field	Texture (?)
1	No	298	0	0	No
2	No	298	10	0	No
3	No	77	0	0	No
4	Yes	77	0	0	No
5	No	77	10	0	Yes, $\uparrow 00\text{L}$
6	Yes	77	10	0	Yes, $\uparrow 00\text{L}$
7	Yes	77	10	45°	Yes, $\uparrow 00\text{L}$

Figure Captions

Figure 1. Orientation of specimen holder in magnetic field. Field is

a) 0° to the holder surface; b) 45° to the holder surface.

Figure 2. X-ray diffraction patterns for $\text{Ba}_2\text{YCu}_3\text{O}_{7-x}$ powder exposed to

a) 10 kG field at 0° rotation in liquid nitrogen (Samples 5 and 6), b) no field (Sample 1; patterns for Samples 1-4 were identical), and c) 10 kG field at 45° rotation in liquid nitrogen (Sample 7). (Cu $K\alpha$ radiation)

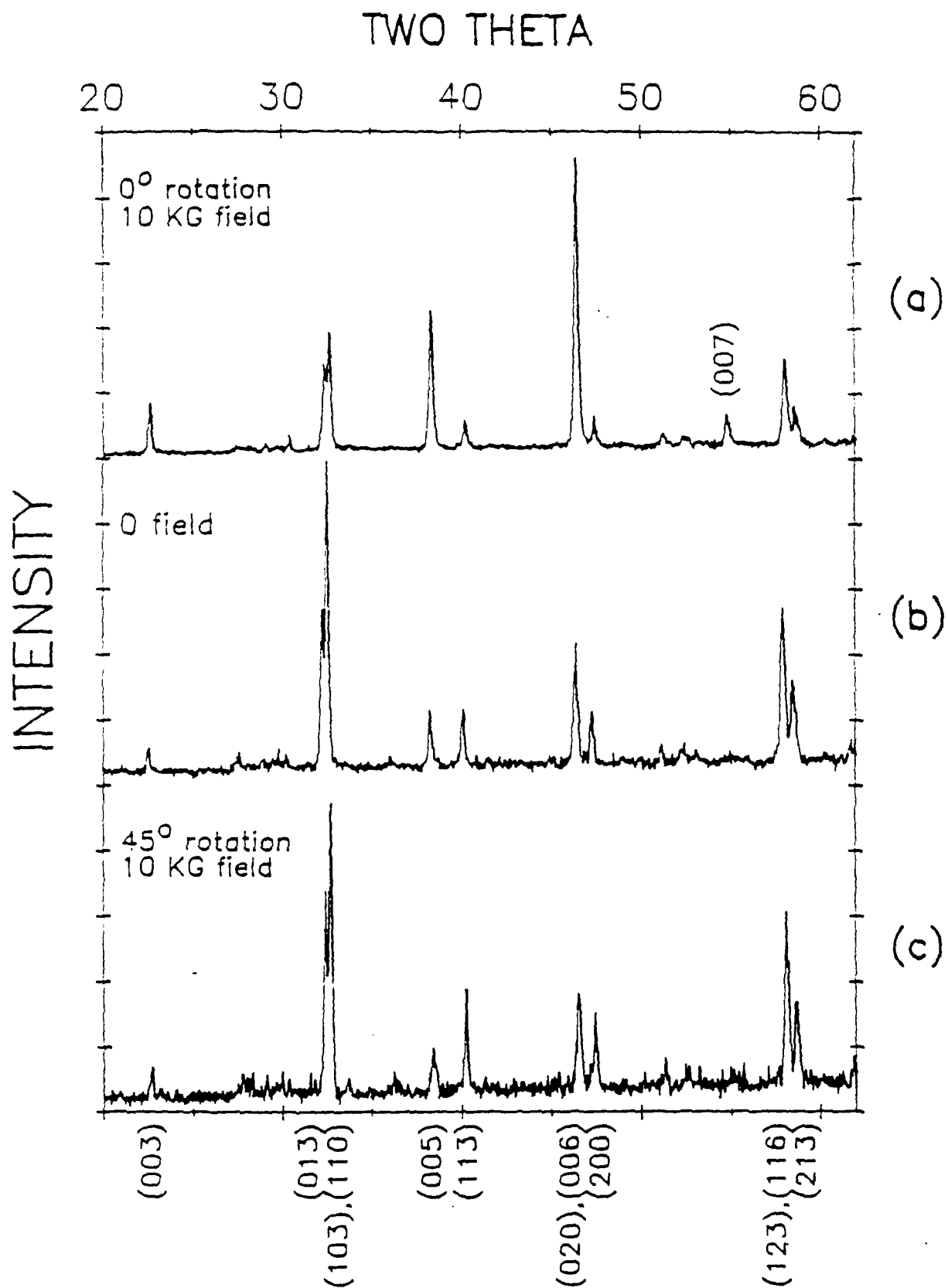


Fig. 1

JUL 06 1988

Reaction of $\text{Ba}_2\text{YCu}_3\text{O}_{6.9}$ Films with Yttria-Stabilized Zirconia Substrates

M.J. Cima, J.S. Schneider, and S.C. Peterson

Ceramics Processing Research Laboratory, Materials Processing Center, Massachusetts Institute of Technology, Cambridge, MA 02139

W. Coblenz

Norton Company, Northboro, MA 01532

ABSTRACT

Degradation of $\text{Ba}_2\text{YCu}_3\text{O}_{6.9}$ films on yttria-stabilized zirconia substrates is shown to proceed by barium depletion from the film and barium zirconate formation. This process is accompanied by a decrease in the temperature of zero resistivity and ultimately produces $\text{Y}_2\text{Cu}_2\text{O}_5$ and CuO . BaZrO_3 is, however, found to be inert to $\text{Ba}_2\text{YCu}_3\text{O}_{6.9}$ at 950°C . Use of a truly chemically inert substrate material may permit extended heat treatment of films without degradation due to substrate interactions.

Fabricating thin or thick films of high-temperature superconductors on dielectric substrates has become a major challenge to the development of many electronics applications. Because these films are in intimate contact with substrates and have large surface area-to-volume ratios, they are susceptible to contamination from the substrate. The most apparent effect of chemical degradation of the film is a decrease in the temperature of zero resistivity. Frequently, a large drop in resistivity at a temperature near the bulk T_c value is observed, followed by a wide region of low resistance at lower temperatures [1]. To date, this effect has not been quantified and its extent is not yet reproducible, but it is nonetheless apparent in many samples. The typically high process temperatures for film fabrication aggravate the problem because of increased diffusion rates. Steps must be taken to understand the chemical interactions of the films with substrates so that effective diffusion barriers can be developed for reactive substrate materials.

Yttria-stabilized zirconia (YSZ) has been used recently as a substrate for Ba₂YCu₃O_{6.9} (BYC) in both thin- and thick-film fabrication [1-4]. Although YSZ's dielectric behavior does not suit many electronic applications, its refractory nature has led many to believe that its chemical interactions may be sufficiently slow to allow extended thermal treatment of deposited films without significant chemical degradation. For this reason, YSZ has been considered a candidate for use as a diffusion barrier on more reactive substrates [2].

YSZ, however, is not completely inert to BYC: degradation manifests itself as a lower critical temperature for BYC films on YSZ substrates. Recent observations in this area at the NEC Corporation [5] prompted this report of our observations of BYC reactions with YSZ, to discover alternative substrates or possible modifications of zirconia substrates. This communication describes results of experiments indicating 1) the chemical reactions by which BYC films degrade on YSZ substrates and 2) the inertness of one reaction product, BaZrO₃, to BYC at high temperatures, indicating it to be a candidate substrate material.

BYC powder was produced conventionally by calcining barium carbonate (Mallinckrodt, Inc., Paris, KY), yttrium oxide (Atlantic Equipment Engineers, Bergenfield, NJ), and cupric oxide (J.T. Baker Chemical Co., Phillipsburg, NJ). The powder was ball-milled in Freon™ and calcined at 950°C for 60 h.

The YSZ used in this study (Zircar Products, Inc., Florida, NY) contained 12 wt% yttria. Substrates were fabricated by cold pressing this powder in 0.75-inch dies and sintering at 1600°C for 4 h. The substrate surfaces were polished with a 30- μ m diamond-embedded polishing wheel for 5 min, then with 1- μ m diamond paste and kerosene for 10 min.

Films were cast from a suspension of BYC powder dispersed in toluene with Menhaden fish oil onto substrates using a method developed by Adams [6]. As toluene is volatile, casting was performed beneath a crystallization dish to reduce the evaporation rate. The films were sintered in flowing oxygen for 5, 10, 15, or 60 min, or 12 h by insertion directly into a 950°C furnace. The film thickness was controlled by adjusting the powder concentration in the toluene and repeatedly applying this dispersion. The final film thickness after firing was approximately 10 μ m.

Composite BYC-YSZ and BYC-BaZrO₃ samples (BaZrO₃ obtained from Harshaw Chemical Co., Cleveland, OH) were fabricated to contain nominally 50 vol% BYC with 50 vol% YSZ or BaZrO₃. These compositions were chosen to maximize the interfacial area between the reactants and, therefore, the degree to which reaction can occur at a given temperature. The powders were mixed dry, pressed in a 0.5-inch die, and sintered in a manner similar to that used to prepare the thick films. X-ray diffraction (XRD) patterns of the composite samples and thick films were obtained using Cu(K α) radiation. A.C. susceptibility of the composite samples was measured at 1000 Hz.

Examination of the composite BYC-YSZ samples by XRD after heat treatment indicated that all samples had identical patterns, regardless of sintering time (Fig. 1). Also, no reflections could be indexed to orthorhombic or tetragonal BYC. The reflections were, however, consistent with the presence of cubic ZrO₂, BaZrO₃, CuO, and Y₂Cu₂O₅. These results indicate that the BYC completely decomposed to BaZrO₃ in the presence of ZrO₂. The overall chemical reaction can be represented as:



The driving force for this reaction is provided by the high chemical stability of BaZrO₃. The reaction between BYC and YSZ thus appears to proceed by barium removal from the BYC, yielding yttrium- and copper-rich material. This simple picture is consistent with the known phase be-

havior of the Ba-Y-Cu-O system investigated by Roth *et al.* [7]. Figure 2 shows the phase diagram of this system, indicating that near 900°C, ternary equilibria exist between the Ba₂YCu₃O_{6.5}, CuO, and BaY₂CuO₅ phases, as well as between BaY₂CuO₅, CuO, and Y₂Cu₂O₅. Barium oxide extraction from Ba₂YCu₃O_{6.5} requires the overall composition to proceed along the line marked A-A' in Figure 2. If local thermodynamic equilibrium in the film is maintained throughout this process, the extraction proceeds with the formation of CuO and a transient appearance of BaY₂CuO₅, followed by Y₂Cu₂O₅ formation. Thus, the primary degradation mechanism involves barium loss from the film rather than film contamination by substrate material.

Several thick films were also examined by XRD. The patterns observed were consistent with the phase diagram, as shown in Figure 3. Since these films were only partially reacted, BaY₂CuO₅ is present. A reaction layer is apparent in Figure 4, a scanning electron microscopic image of a BYC-YSZ thick-film fracture surface. This film had been heat-treated for 6 h at 950°C and showed significant degradation at the critical temperature, as did all films heat-treated for extended periods. The final state, of course, is consistent with that observed in the composite samples. Note that the path described in Figure 2 passes through that region of overall composition assigned by Roth *et al.* in which partial melting is observed at temperatures above 890°C. The implied presence of a liquid phase suggests that the reaction proceeds rapidly after enough barium has been extracted to yield an overall composition in the region of partial melting.

The BYC-BaZrO₃ composite samples showed no phase composition change even after heat treatment at 950°C for 30 min. Figure 5 shows the initial XRD pattern and a pattern observed after 30 min at 950°C. All reflections are indexed in the figure according to those expected for BaZrO₃ and BYC. The samples were tested for the presence of superconducting material after heat treatment in oxygen at 400°C.

The samples' unexpectedly high resistance at room temperature prevented conventional four-point resistance measurement. A.C. susceptibility measurements, however, confirmed the presence of superconducting Ba₂YCu₃O_{6.9}. These measurements were made by filling the sample tube of the susceptometer with powder obtained by crushing the composite samples. An equivalent volume of pure BYC was calculated on the basis of the initial fraction of BYC in the composite. The

equivalent volume of pure BYC could then be used to gauge the degradation of BYC in contact with BaZrO₃ by comparing the magnitude of a.c. signals in the susceptometer.

Figure 6 compares the a.c. signal obtained from BYC contained in a reacted BYC-BaZrO₃ composite fired for 30 min at 950°C with the signal obtained from an equal volume of pure BYC powder. The magnitude of the signal below the transition temperature is unchanged (within experimental error) by heat treatment in the presence of BaZrO₃. The susceptibility measurement for an equivalent volume of BYC in a zirconia composite shows no indications of superconductivity after 5 min at 950°C (Fig. 6).

These results indicate that BYC is stable in contact with BaZrO₃ at temperatures as high as 950°C. Also, because no significant degradation occurred under the most stringent conditions for chemical reaction, we can conclude that the solubility of yttrium and copper in BaZrO₃ is minimal. Clearly, these observations suggest that BaZrO₃ is a potential substrate material for use with BYC films. The possible importance of these results prompts us to report them before BaZrO₃ substrate fabrication.

Ceramics within the Ba-Sr-Ca zirconate system have served as microwave dielectrics [8, 9], suggesting that BaZrO₃ substrates may suit applications requiring the low surface resistance of superconductors at high frequency. Unfortunately, microwave dielectric losses have been shown to increase with increasing barium content in zirconate dielectrics [9].

Superconducting BYC thick films were applied to YSZ substrates. The reactions between BYC and YSZ were analyzed by XRD analysis. It was observed that the BYC completely degrades in the presence of ZrO₂ to form BaZrO₃, CuO, and Y₂Cu₂O₅, with BaY₂CuO₅ present as a transient phase.

BaZrO₃ was found to be largely inert toward reaction with Ba₂YCu₃O_{6.9}, even at elevated temperatures, suggesting that BaZrO₃ could be important as an inert substrate for BYC film fabrication.

ACKNOWLEDGMENTS

This research was funded by the Defense Advanced Research Projects Agency. The authors gratefully acknowledge helpful discussions with Professors D. Rudman and R. Rose.

REFERENCES

1. M. Naito, R.H. Hammond, B. Oh, M.R. Hahn, J.W.P. Hsu, P. Rosenthal, A.F. Marshall, M.R. Beasley, T.H. Geballe, A. Kapitulnik, *J. Mat. Res.*, **2** [6] 713 (1987).
2. M. Gurvitch and A.T. Fiory, *Appl. Phys. Lett.*, **51**, 1027 (1987).
3. H. Koinuma, T. Hashimoto, M. Kawasaki, and K. Fueki, *Jpn. J. Appl. Phys. (Eng.)*, **26**, L399 (1987).
4. H. Koinuma, T. Hashimoto, M. Kawasaki, K. Kitazawa, K. Fueki, A. Inoue, and Y. Okabe, Proceedings of the Society of Photo-Optical Instrumentation Engineers, Newport Beach, CA, 1988 (in press).
5. Junji Tabuchi, Atsushi Ochi, Kazuaki Utsumi, and Masatomo Yonezawa, *Nippon-Seramikkusu-Kyokai-Gakujutsu-Ronbunshi (Eng.)*, **96** [4] 450-54 (1988).
6. R.W. Adams, MS thesis, Department of Materials Science and Engineering, MIT, Cambridge, MA, pp. 20-21, February 1987.
7. R.S. Roth, K.L. Davis, and J.R. Dennis, *Adv. Ceram. Matls.*, **2** [3B] 303-12 (1987).
8. R.C. Kelly, A.C. Greenham, and G.C.E. Olds, *J. Am. Ceram. Soc.*, **56** [7] 352-54 (1973).
9. H. Ouchi and S. Kawashima, *Jap. J. Appl. Phys.*, **24**, 60-64 (1985).

FIGURES

Figure 1. XRD pattern of a composite BYC-YSZ pellet.

Figure 2. Schematic showing BYC reaction with YSZ to form BaZrO₃.

Figure 3. XRD pattern of a BYC thick film on a YSZ substrate.

Figure 4. BYC film heat-treated for 6 h at 950°C. Interface shows BaZrO₃, BaY₂CuO₅, and Y₂Cu₂O₅.

Figure 5. BYC-BaZrO₃ composite x-ray diffraction patterns a) before and b) after heat treatment at 950°C for 30 min.

Figure 6. A.C. susceptibility for initially equal volumes of BYC in composite samples of BYC-BaZrO₃ and BYC-YSZ (each plot is offset by one unit on y axis to facilitate sample comparison).

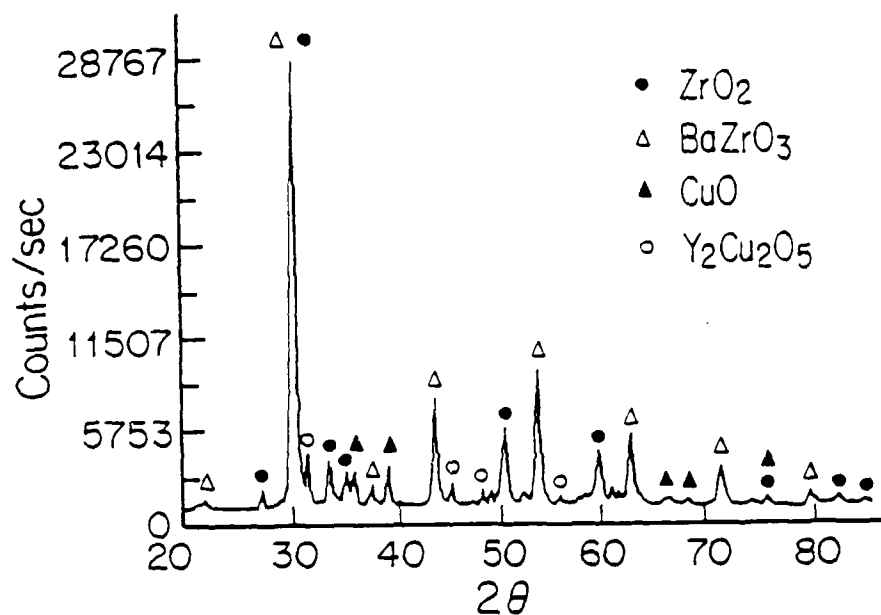


Figure 1. XRD pattern of a composite BYC-YSZ pellet.

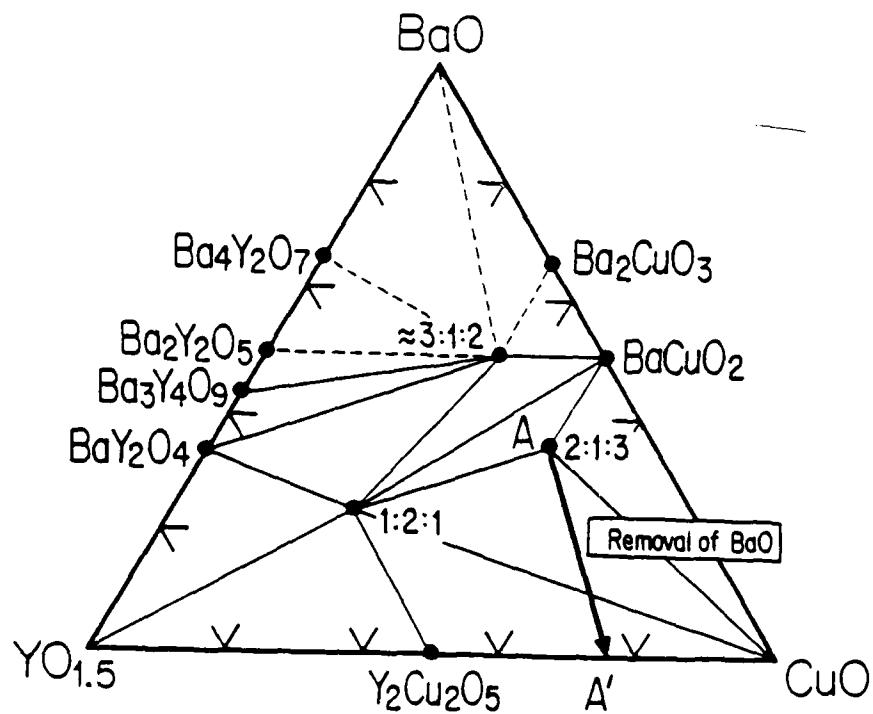


Figure 2. Schematic showing BYC reaction with YSZ to form BaZrO₃.

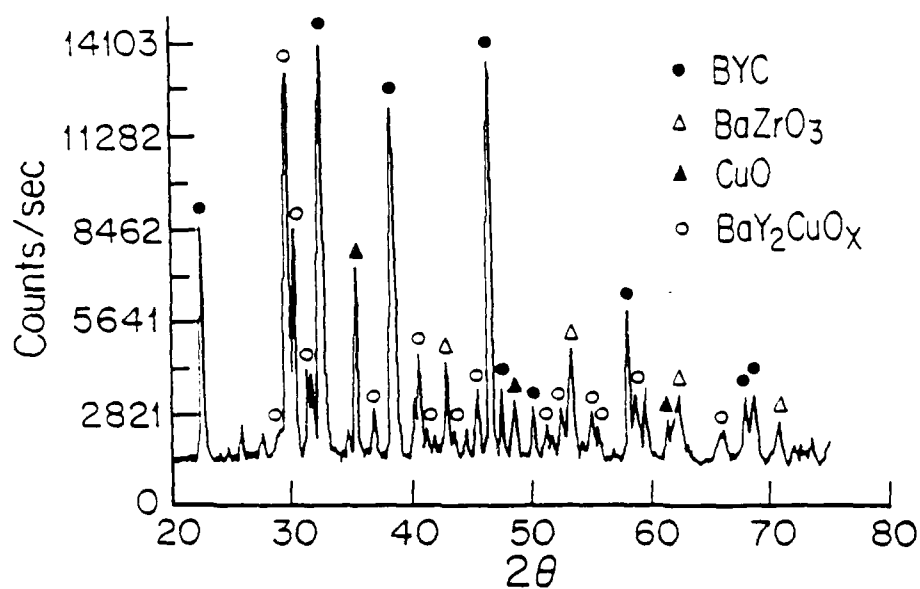


Figure 3. XRD pattern of a BYC thick film on a YSZ substrate.

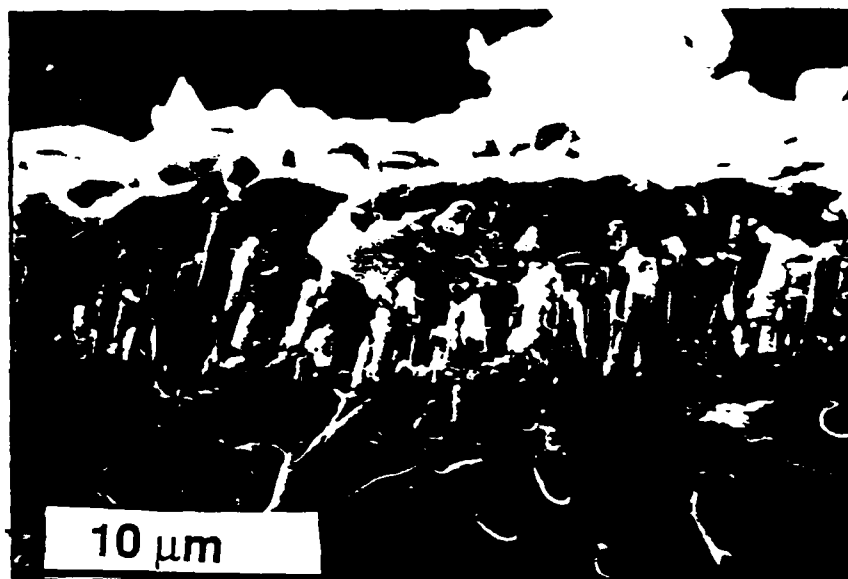


Figure 4. BYC film heat-treated for 6 h at 950°C. Interface shows BaZrO₃, BaY₂CuO₅, and Y₂Cu₂O₅.

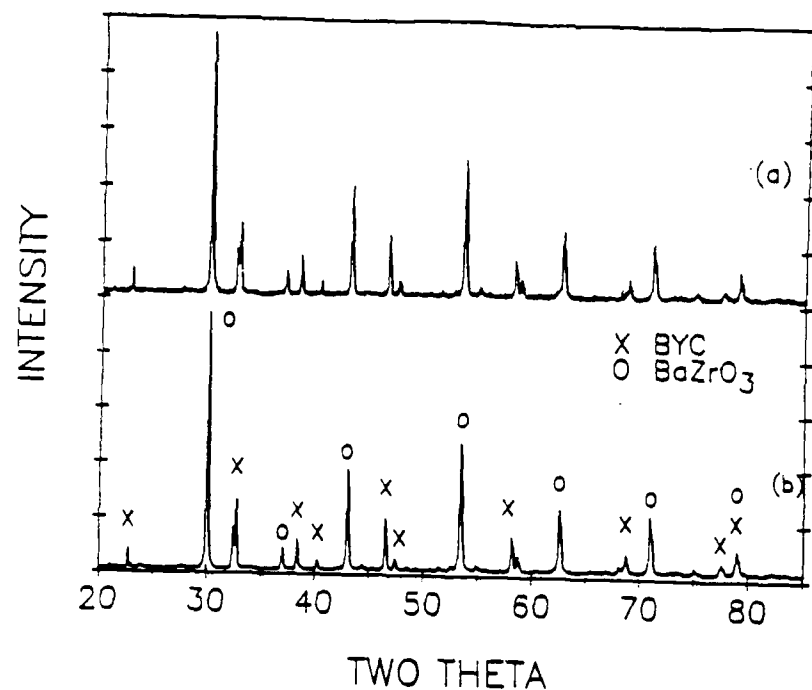


Figure 5. BYC-BaZrO₃ composite x-ray diffraction patterns a) before and b) after heat treatment at 950°C for 30 min.

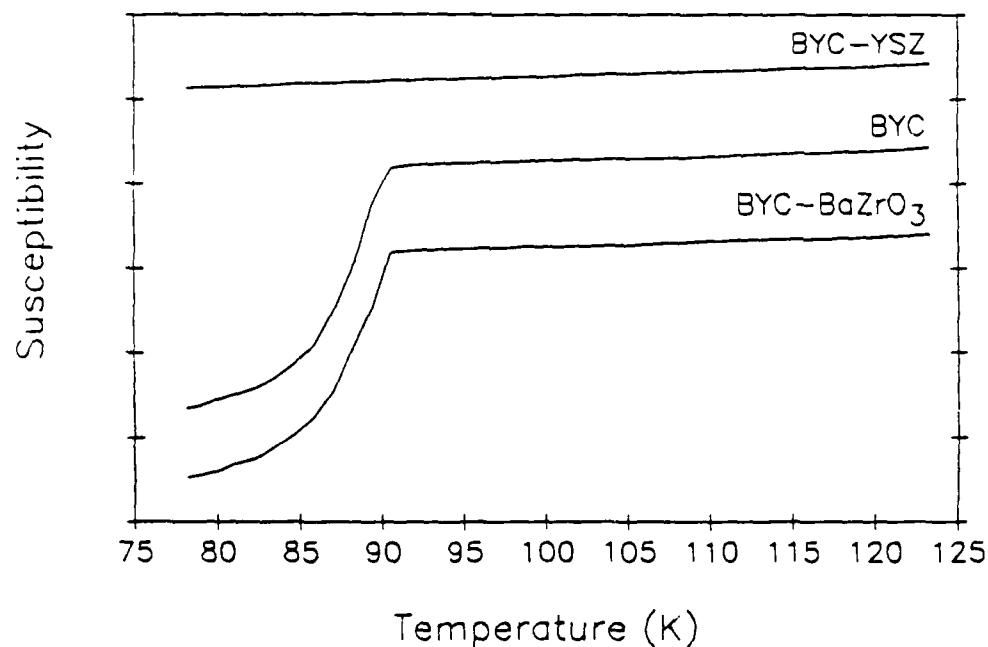


Figure 6. A.C. susceptibility for initially equal volumes of BYC in composite samples of BYC-BaZrO₃ and BYC-YSZ (each plot is offset by one unit on y axis to facilitate sample comparison).

2. SYNTHESIS OF $\text{Ba}_2\text{YCu}_3\text{O}_{6.9}$ POWDER

Raymond C. Chiu, Michael J. Cima, and Wendell E. Rhine

ABSTRACT

A barium-yttrium-cuprate superconductor precursor was obtained by spray drying a nitrate solution of barium, yttrium, and copper. It was found that the spray-dried precursor powder consisted of two phases and had an overall composition of $\text{Ba}_2\text{YCu}_3(\text{NO}_3)_4(\text{OH})_9 \cdot 13.5\text{H}_2\text{O}$. Upon calcination of the precursor powder to 810°C , a nonsuperconducting tetragonal BYC phase was observed. Upon further calcination at 950°C , the superconducting BYC phase was obtained. The resulting BYC powder was also found to be copper deficient due to impurities in the starting copper nitrate powder.

INTRODUCTION

The method most used to prepare $\text{Ba}_2\text{YCu}_3\text{O}_{7-x}$ (BYC) superconductor powder involves a solid-state reaction between Y_2O_3 , CuO , and BaCO_3 . In this method, the decomposition of BaCO_3 is thought to be the rate-limiting step. For this reason and because it is difficult to achieve an intimate mixture of precursor powders by dry mixing, long calcination times and calcination temperatures in excess of 900°C are required. Another common approach to BYC preparation involves the coprecipitation of basic carbonates. In this method, good chemical homogeneity is achieved, but the decomposition of BaCO_3 is still difficult. With either approach, the powder morphology cannot be controlled and the nature of the decomposition chemistry introduces large amounts of residual carbon. This carbon contamination is known to be one of the factors responsible for the degradation of critical current density that occurs as carbon forms a semiconductive layer at the grain boundaries (Nakahara *et al.*, 1988).

In an earlier attempt to control powder morphology, a sol-gel-emulsion technique was investigated for BYC powder preparation (Chiu, Cima, and Rhine, 1988). Although it was demonstrated that powder morphology could be controlled, complete removal of possible carbon contaminants (surfactants and/or gellation agents) was difficult.

In the current study, a BYC superconductor precursor was obtained by spray drying an aqueous nitrate solution of barium, yttrium, and copper. The advantages of this method are: 1) minimal carbon contamination, 2) the process is simple, and 3) the process may allow control of powder morphology. Figure 1 compares the carbon content found in precursors produced by spray drying, by freeze drying, and by a sol-gel-emulsion technique

(analysis performed by LuVak Inc.). During this research period, the spray-dried nitrate precursor was characterized and its decomposition to the oxide studied.

EXPERIMENTAL PROCEDURE

The aqueous solution used for spray drying was prepared by dissolving stoichiometric amounts of $\text{Ba}(\text{NO}_3)_2$, $\text{Y}(\text{NO}_3)_3$ (made by reacting Y_2O_3 with nitric acid), and $\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$ in water. The solution was fed into the spray drier at a rate of 3 L/h. The inlet temperature was held in excess of 335°C . The powder was calcined under an oxygen atmosphere in MgO crucibles.

RESULTS AND DISCUSSION

A scanning electron micrograph (SEM) of the precursor powder is shown in Figure 2a. The size of the particles appeared to range from 5 to $20\text{ }\mu\text{m}$. (Improvements in the particle size and the particle size distribution can be achieved with a more sophisticated atomizer.) Upon calcination to 810°C , little agglomeration was observed (Fig. 2b). The particles also seemed to have shrunk and appeared to be highly porous. After 8 h of milling with tungsten-carbide media, an average particle size of $0.63\text{ }\mu\text{m}$ was obtained.

The thermogravimetric analysis (TGA) plot in Figure 3 shows that a total weight loss of 45% occurred upon heating the precursor to 950°C at a heating rate of $10^\circ\text{C}/\text{min}$ in flowing oxygen. Comparing the derivative of the TGA (DTG) with the differential thermal analysis (DTA) of the precursor (both in Fig. 3), all the weight-loss events appear to coincide with thermal events. This suggests the absence of melting during decomposition, unless such melting occurs simultaneously with a weight loss. The morphology of the calcined powder (Fig. 2b) indicates the absence of melting.

Since the individual metallic nitrates are known to start decomposing at temperatures less than 300°C , it is expected that the precursor powder was partially reacted during spray drying. Indeed, the implicit formula deduced by chemical analysis (Galbraith Labs, Inc.) for the spray-dried powder is $\text{Ba}_2\text{YCu}_3(\text{NO}_3)_4(\text{OH})_9 \cdot 13.5\text{H}_2\text{O}$, a basic nitrate compound. X-ray powder diffraction (XRPD) of the nitrate precursor determined that the powder consisted of a cubic phase and a tetragonal phase (Fig. 4). Neither of the phases, however, was identified to be a single-cation nitrate or a single-cation nitrate intermediate. This suggests that at least two cations are intimately mixed at the molecular level in each

particle. This high degree of chemical homogeneity in the precursor is demonstrated by the single short calcination cycle needed for complete conversion to the oxide.

The most interesting result was found upon calcining the spray-dried precursor to 810°C . The XRPD pattern of this powder (Fig. 5b) is deceptively similar to that of the orthorhombic superconducting phase; this is identical to the result obtained upon calcining the sol-gel derived powder from the previous study (Chiu, Cima, and Rhine, 1988). Further examination confirmed that the powder pattern corresponds to the nonsuperconducting tetragonal (T') phase observed by many researchers for powders derived from coprecipitation from oxalates or from the Pechini method (followed by calcining at 800°C). This T' phase is believed to have a high oxygen content but does not convert to the superconducting orthorhombic phase upon cooling.

Lay (1988) suggests that the T' phase is indeed thermodynamically stable while the orthorhombic phase is metastable. The factors that seem to stabilize the T' phase are still in question, though for methods incorporating carbon, residual carbonates are believed to be stabilizing. Preparation from nitrate solutions seems to have the same effect. These two methods are also similar in that both use aqueous media. Residual water, which may require high temperatures to eliminate from BYC, could also play a role in stabilizing the T' phase.

Nevertheless, upon further calcination of the spray-dried nitrate precursor to 900°C , the desirable tetragonal phase was obtained, which converted to the orthorhombic phase upon cooling (Fig. 5a). Due to overlaps in the diffraction patterns between the T' and orthorhombic phases, however, it is difficult to determine the degree of conversion to the desirable tetragonal phase. Thus, care must be taken in using XRPD for characterizing BYC produced by the nitrate method or by carbon-forming methods.

With the nitrate-solution method, the stoichiometry is also difficult to control. As determined by iodometric titration, the commercially available copper nitrate hydrate ($\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$) was found to have a slightly higher water content than that specified by the manufacturer due to the slightly hygroscopic behavior of the chemical. This can result in a copper deficiency of $1.64 \pm 0.01\%$ in the weight of the copper content. In examining the phase diagram of the system $\text{BaO}-\text{Y}_2\text{O}_3-\text{CuO}_x$, copper deficiency leads to formation of BaCuO_2 and Ba_2YO_5 . In reviewing the diffraction patterns in Figures 5a and 5b, small amounts of impurities are indeed observed; the extra diffraction peaks (circled in the patterns) were identified as diffraction lines for BaCuO_2 and BaY_2CuO_5 . A copper deficiency can also occur when copper is lost during calcination. In the decom-

position of copper nitrate trihydrate, copper basic nitrate, a decomposition intermediate, is known to sublime slowly from 400 to 500°C under vacuum (Taylor, Dollimore, and Gamlen, 1986).

Chemical analyses of precursor powders before and after calcination were therefore performed to determine the cause of copper deficiency (Table 1). The results showed that the spray-dried precursor powder was indeed copper deficient, and that the amount of deficiency could be accounted for by the deficiency in the starting copper nitrate. Due to the estimated error of the chemical analysis employed, however, it was inconclusive whether copper was lost during calcination.

CONCLUSIONS

The spray-dried precursor powder for BYC derived from a nitrate solution of barium, yttrium, and copper was found to consist of two phases and to have an overall chemical formula of $\text{Ba}_2\text{YCu}_3(\text{NO}_3)_4(\text{OH})_9 \cdot 13.5\text{H}_2\text{O}$. The water content, however, was much higher than expected, with a spray-drier exit temperature above 135°C (an error in the nitrogen analysis is suspected). Although the precursor powder was found to be copper deficient, this can be easily corrected by using standardized chemical solutions for spray drying. A large production volume can therefore be implemented in the near future.

REFERENCES

- S. Nakahara, G.J. Fisanick, M.F. Yan, R.B. van Dover, T. Boone, and R. Moore, "On the Defect Structure of Grain Boundaries," to be published in *J. Cryst. Growth*, 1988.
- R.C. Chiu, M.J. Cima, and W.E. Rhine, "Powder Synthesis of $\text{Ba}_2\text{YCu}_3\text{O}_{6.9}$," CPRL Report #R14, MIT, pp. 45-52 (1988).
- K.W. Lay, "High-Temperature Superconductors — Oxygen Ordering in $\text{YBa}_2\text{Cu}_3\text{O}_x$," General Electric Research and Development #N00014-87-C-0798 (1988).
- T.J. Taylor, D. Dollimore, and G.A. Gamlen, "Deauration and Denitration Studies on Copper Nitrate Trihydrate," *Thermochimica Acta*, 103, 333-40 (1986).

Table 1. Chemical analysis of the spray-dried nitrate powder before and after calcination.

Powder	Amount of Each Element (wt%)			
	Ba	Y	Cu	N
Pre-calcined	23.09 ± 0.35	7.34 ± 0.11	15.57 ± 0.23	4.75
Calcined (950°C)	42.51 ± 0.64	13.99 ± 0.21	21.68 ± 0.42	0.01

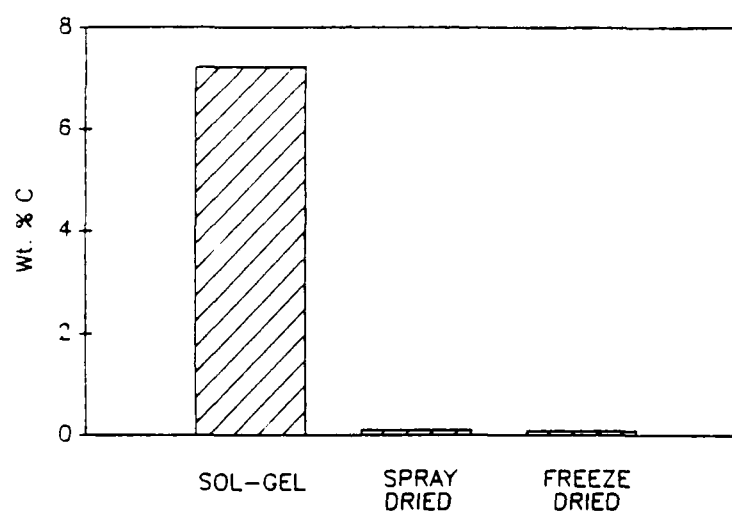


Figure 1. A comparison of carbon content in BYC powder derived from various types of nitrate precursors.

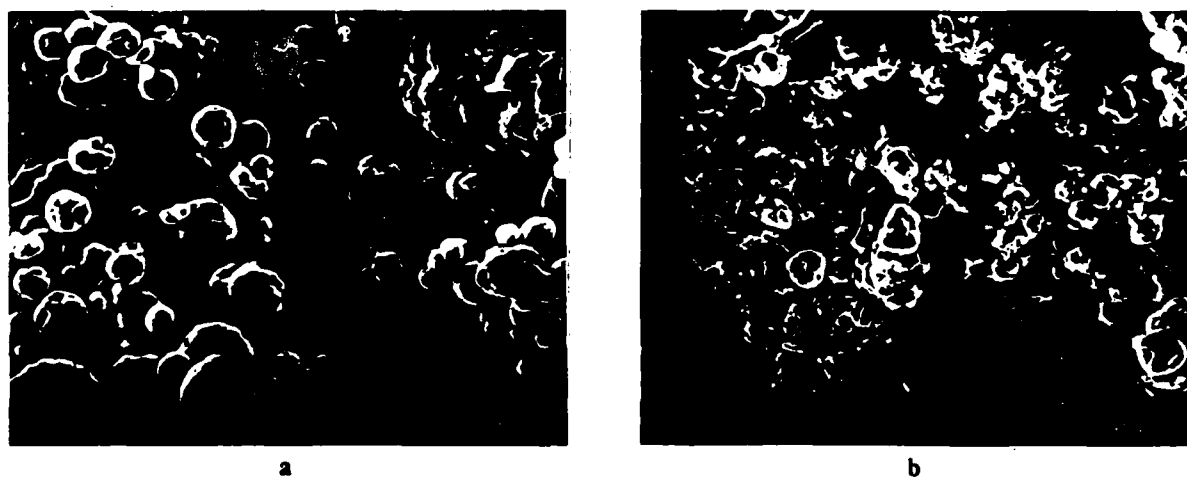


Figure 2. SEMs of a) the spray-dried nitrate precursor powder, and b) the spray-dried nitrate precursor powder after calcination at 810°C .

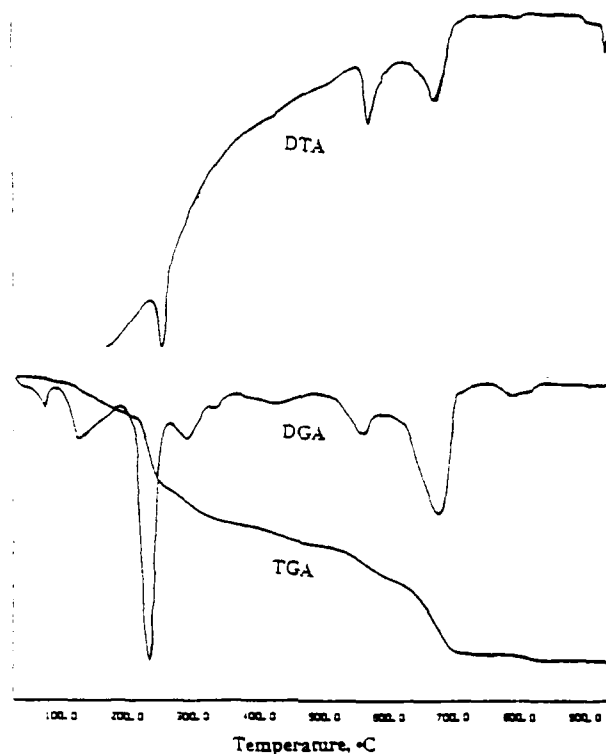


Figure 3. TGA, DGA, and DTA plots of the nitrate precursor.

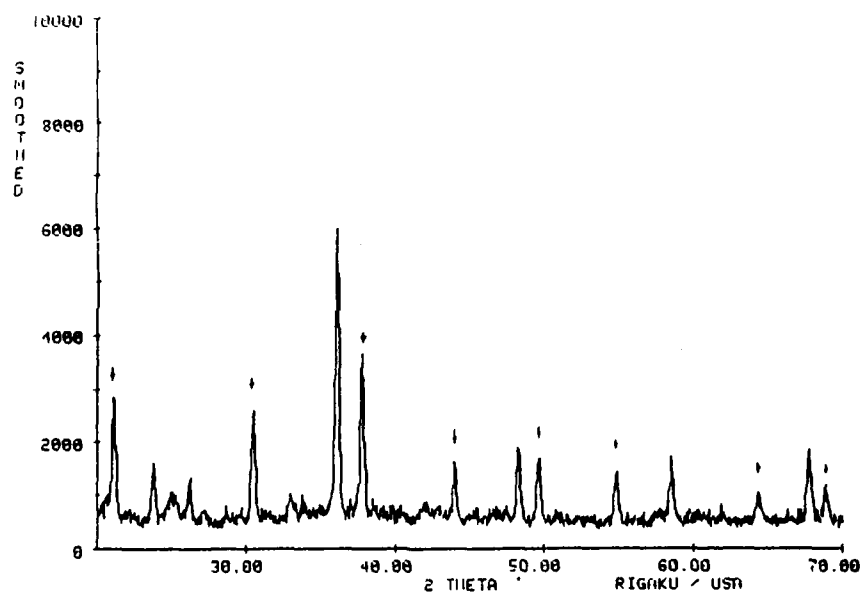


Figure 4. XRPD pattern of the nitrate precursor powder. The arrows indicate diffraction lines for the cubic phase.

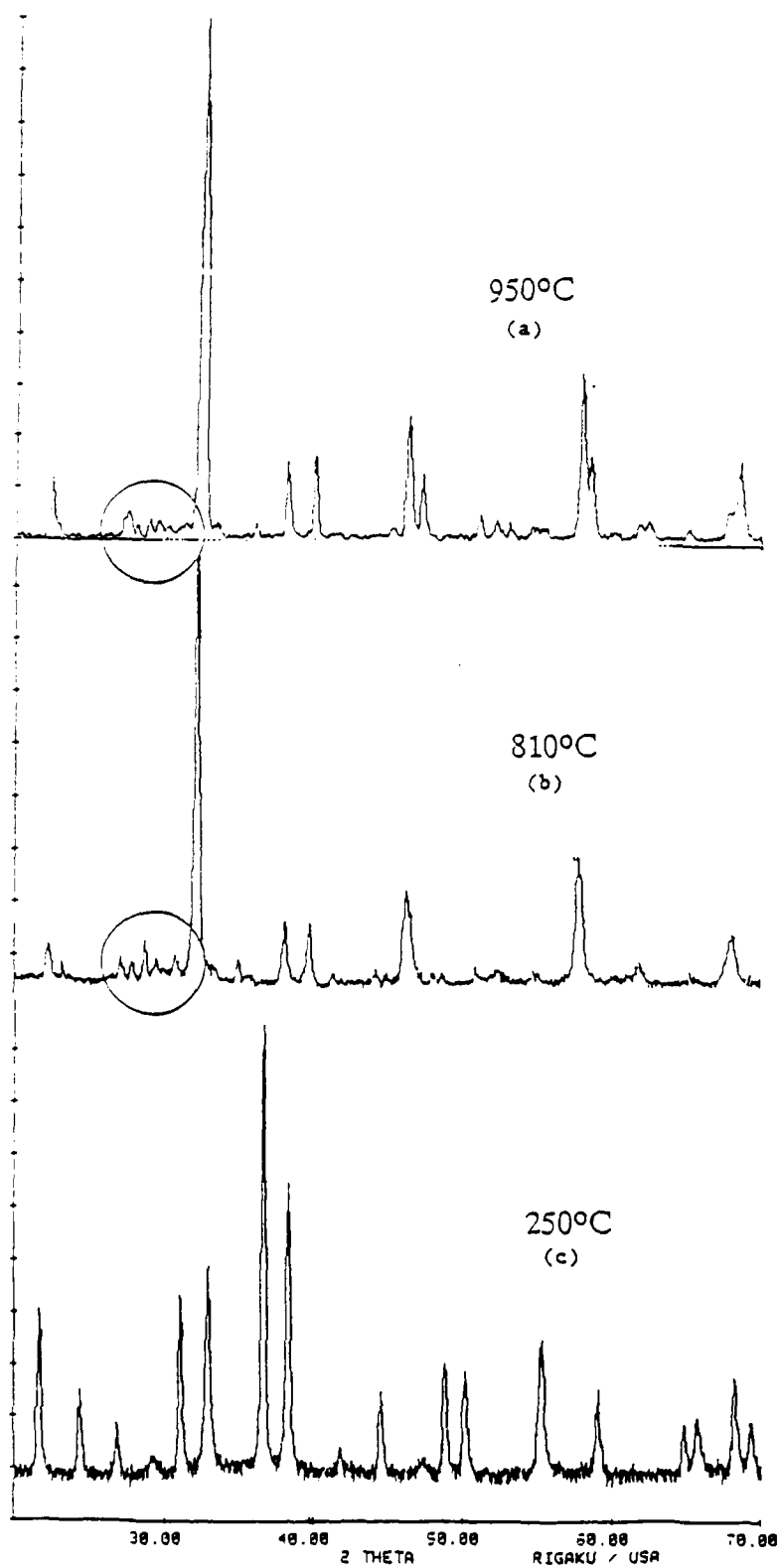


Figure 5. XRPD patterns of the precursor powder calcined at a) 950°C, b) 810°C, and c) 250°C.